

Docket No. RID 01058RemarksAmendments to the claims

Claims 1 and 5 have been amended to include an upper limit on the void volume (see paragraph 0025). Claim 1 has additionally been amended to recite a particular shape for the elastomer composite pieces (see paragraph 0021). Claims 3 and 4 have been amended to make them independent claims, including the limitations regarding the void volume. Claims 3, 4, and 5 have been amended to recite that the elastomer composite is produced by a wet masterbatch method (see paragraphs 0012 and 0013). Claims 2 and 6-8 have been cancelled. Claim 65 has been added and is supported by the specification as originally filed. No new matter is entered by these amendments.

Examiner Interview

The undersigned thanks the Examiner for taking the time to discuss the Jorgensen reference on September 6, 2007.

The Jorgensen Reference Teaches Away From The Recited Void Volume

Jorgensen discloses "Bales having a density change of *greater than about two times* that of the original particulate rubber are found to be *not friable...*" (column 4, lines 43-44, italics added). The table below lists samples from Jorgensen, along with the void volume calculated as discussed in the Response to Office Action dated July 19, 2007. All the information in the table except for the void volume is drawn directly from Jorgensen; the void volume is calculated using data from the Jorgensen patent.

Docket No. RID 01058

Sample Number	Mooney Viscosity	Times Increase in Bulk Density	Void Volume (%)	Friable?
Example 1, Sample 1	80	1.43	43	Yes
Example 1, Sample 2	80	1.59	37	Yes
Example 1, Sample 3	80	1.65	35	Yes
Example 1, Sample 4	80	1.84	27	Yes
Example 1, Sample 5	80	1.97	23	Yes
Example 1, Sample 6	80	2.3	9.5	NO
Example 2, Sample 1	50	1.4	33	Yes
Example 2, Sample 2	50	1.46	30	Yes
Example 2, Sample 3	50	1.46	30	Yes
Example 2, Sample 4	50	1.58	24	Yes
Example 2, Sample 5	50	1.64	21	NO
Example 2, Sample 6	50	1.89	9.5	NO

The claims, as amended, recite that the void volume of the bale should be from 3% to 20% by volume. Jorgensen teaches away from this void volume range because he discloses that a bale having a void volume in this range is not friable. As can be seen from the table, while Jorgensen discloses bales having a density in the range recited by the pending claims, Jorgensen also discloses that these bales are not suitable for the use contemplated by Jorgensen.

Jorgensen Fails To Contemplate Rubber Particles Having The Recited Shapes

The claims recite specific shapes for the particles in the bale. Applicant submits that Jorgensen discloses compressing powders or crumbs made up of relatively equiaxed particles (e.g., with diameters between about 0.1 mm and about 15 mm; see column 2, line 8). Jorgensen fails to disclose that the particles of rubber may have an aspect ratio or what that aspect ratio might be. In

Docket No. RID 01058

contrast, for example, claim 3 recites that the elastomer composite pieces are in generally planar form; claim 4 recites short strips. Such anisotropic particles will compress differently than the equiaxed particles disclosed by Jorgensen whether they are compressed hydrostatically or uniaxially. Indeed, the compression factor emphasized by Jorgensen (e.g., a factor of 1.3-2), may not be appropriate for describing the compression of elongated pellets or strips, since, for a given magnitude of compression, the resulting porosity may vary depending on the direction of compression. Applicant submits that the processes described by Jorgensen do not teach a skilled artisan the appropriate magnitude of compression or porosity of a bale that is formed from non-equiaxed particles.

Jorgensen Fails To Contemplate Rubbers Having The Claimed Mooney Viscosity

The claims recite that the elastomer composite has a Mooney viscosity of at least 100. Jorgensen discloses rubbers having Mooney viscosities of 50 and 80. At the time of the Jorgensen patent, elastomer composites were produced by a "dry mix" method in which dry filler is mixed with dry rubber. However, the dry mix method of combining filler with rubber breaks polymer chains, reducing the molecular weight of the rubber and therefore its Mooney viscosity. Our commonly owned patent, 6,048,923, presents a different method of combining filler and elastomer in which an aqueous slurry of filler is combined with an aqueous emulsion of elastomer. Wet masterbatch methods such as those disclosed in the '923 patent results in elastomer composites having a higher Mooney viscosity than either the raw polymer or composites produced using a dry mix method (see p. 389 of Wang, et al., NR/Carbon Black Masterbatch Produced with Continuous Liquid Phase Mixing, KGK Kautschuk Gummi Kunststoffe, 7-8/2002, page 388-396, a copy of which is attached as Exhibit A). Dry mix methods such as those disclosed by Jorgensen are unlikely to produce rubber composites having a Mooney Viscosity greater than 100, as recited in the claims. Furthermore, even for less viscous rubbers, Jorgensen suggests that void volumes below 21% render the bale non-processable. As a result, Applicant submits that Jorgensen fails to disclose or suggest a bale of elastomer composite pieces produced by mixing an elastomer latex with filler wherein the bale has a void volume of from 3 to 20%, as recited by the claims.

Jorgensen Fails To Contemplate Rubbers Produced Using a Wet Masterbatch Method


Wet masterbatch methods, in which elastomer latex is combined with filler, as recited in

Docket No. RID 01058

claims 3, 4, and 5, and the specific wet masterbatch method recited in claims 1 and 65 are not contemplated by Jorgensen. Rather, Jorgensen only discusses dry methods of combining latex with filler. As noted above, dry mix methods reduce the Mooney Viscosity of the resulting rubber. As a result, the elastomer composites recited in the claims have a higher Mooney Viscosity than those disclosed or suggested by Jorgensen. Jorgensen neither discloses nor suggests how rubbers having such a high Mooney Viscosity should be baled. Furthermore, even for less viscous rubbers, Jorgensen suggests that void volumes below 21% render the bale non-processable. As a result, Applicant submits that Jorgensen fails to disclose or suggest a bale of elastomer composite pieces produced by mixing an elastomer latex with filler wherein the bale has a void volume of from 3 to 20%, as recited by the claims.

A Supplemental Information Disclosure Statement and a Request for Continued Examination are submitted herewith. As amended, the application has five independent claims. The application was filed with five independent claims. Therefore, Applicant submits that no further fees are due. Nonetheless, please charge any fees that may be required and refund any overpayment to our Deposit Account 03-0060.

Sep 12, 2007
Date


Valarie B. Rosen
Reg. No. 45,698
Cabot Corporation
157 Concord Road
Billerica, MA 01821
(978) 663-3455

Supp OAR Sep2007.doc

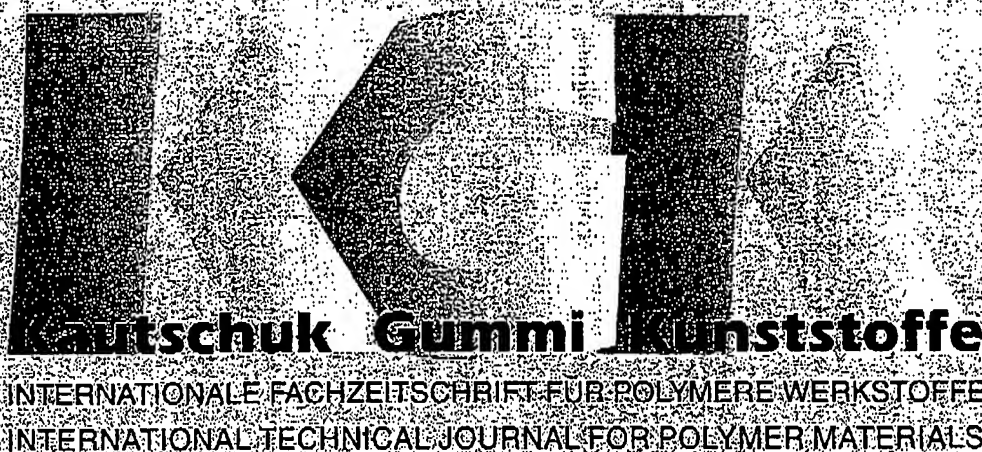


Exhibit A

NR/Carbon Black Masterbatch Produced with Continuous Liquid Phase Mixing¹

M.-J. Wang, T. Wang, Y. L. Wong, J. Shell and K. Mahmud,
Billerica, Massachusetts (USA)

ELASTOMERE UND KUNSTSTOFFE

ELASTOMERS AND PLASTICS

Filler-NR masterbatches · continuous liquid mixing · polymer-filler interaction · filler dispersion · hysteresis · cut-chip resistance · abrasion resistance

The first filler-NR master-batch made with a continuous liquid mixing process is described. The master-batch is produced by fast mixing and mechanical coagulation of polymer with filler, and with very short exposure to high temperature. This achieves excellent performance for the material such as (i) polymer-filler interaction is well preserved, (ii) polymer degradation is essentially eliminated, (iii) superior filler dispersion independent of filler morphology, (iv) simplified mixing with low energy consumption, (v) dust-free operations. The technology enables a wide range of carbon blacks to be used in rubber. Significant improvements in vulcanizate properties are achieved including reduced hysteresis, improved cut-chip resistance and flex-fatigue life and increased abrasion resistance at high filler loading, compared with their dry-mixed counterparts.

NR/Rußmasterbatch Herstellung durch einen kontinuierlichen Misch- und Fällprozess

Füllstoff-NR-Master-batches · kontinuierliches Flüssigphasenmischen · Polymer-Füllstoff-Wechselwirkung · Dispersion · Hysterese · Stollenausbruchverhalten · Abriebwiderstand

Erstmalig wird die Herstellung von Füllstoff-NR Master-batches durch einen kontinuierlichen Misch und Fällprozess des Polymerlatex mit Ruß vorgestellt. Durch das sehr schnelle Mischen und die mechanisch induzierte Koagulation wird ein hoher Dispersionsgrad bei gleichzeitig geringer Temperaturbelastung erreicht. Dieses führt zu ausgezeichneten Materialeigenschaften wie (i) intensive Polymer-Füllstoff-Wechselwirkung, (ii) geringer Polymerabbau, (iii) höhere und morphologieunabhängige Füllstoffdispersion, (iv) vereinfachter Mischprozess bei niedrigerem Energieverbrauch, (v) staubfreie Verarbeitungsabläufe. Die Technologie ist auf eine breite Palette von Rußen anwendbar. Signifikante Verbesserungen der Vulkanisateigenschaften wurden durch diese Füllstoff-NR-Master-batches beispielsweise

NR/Carbon Black Masterbatch Produced with Continuous Liquid Phase Mixing¹

M.-J. Wang, T. Wang, Y. L. Wong, J. Shell and K. Mahmud, Billerica, Massachusetts (USA)

From a processing point of view, mixing is the most critical process for rubber compounding. Along with the basic physical changes of the materials, in some cases chemical reactions, the primary functions of mixing are incorporation, dispersion and distribution of the filler and other ingredients in the polymers. Traditionally, this is achieved by using batch mixing and continuous mixing of fillers and solid rubber or pellets, referred to as dry mixing.

During last few decades, a great effort has been made to produce carbon black-polymer masterbatches by mixing polymer latex with filler slurry and then coagulating the mixture chemically. The commercial products are exclusively made by a batch process. With this process, generally the filler dispersion can be improved relative to dry mixing. However, the long mixing and coagulation time reduces the productivity. For natural rubber as some non-rubber substances in NR latex, protein in particular, can be adsorbed on the filler surface and interfere with polymer-filler interaction.

Cabot Elastomer Composite is a NR-carbon black masterbatch produced with a unique continuous liquid phase mixing/coagulation process [1]. During this process, carbon black incorporation, dispersion and distribution are completed in a very short period of time. It has been found that this liquid phase mixing offers the following benefits over the conventional dry mixing and wet batch processing:

- Simplified mixing procedure;
- Reduced mixing costs due to reduced mixing equipment, energy and labor;

- Elimination of free carbon black handling and reduced dust emission;
- Excellent dispersion of filler independent of filler morphology;
- Improved vulcanizate properties;
- Improved capital efficiency; and
- Facilitation of continuous mixing.

In this paper, after introduction of the production processes of CEC, the processability and physical properties of this material will be discussed in comparison with dry mixing.

Process of CEC production

The process of CEC production, as presented in Figure 1, consists of carbon black slurry make-up, NR latex storage, mixing and coagulation of carbon black slurry and latex, dewatering of the coagulum, drying, finishing and packaging.

The carbon black slurry is prepared by finely dispersing carbon black in water mechanically without any surfactant. The slurry is injected into the mixer at very high speed and mixes continuously with NR latex stream. Under highly energetic and turbulent conditions, the mixing and coagulation of polymer with filler is completed mechanically at room temperature in less than 0.1 second, without the aid of chemicals.

After dewatering of the coagulum in an extruder, the material is continuously fed into the dryer to further reduce the moisture to less than 1 %. The residence time in the dryer is 30 ~ 60 seconds. Over the entire drying process, only for a very short period, typically 5 ~ 10 seconds, will the compound temperature reach 140 ~ 150 °C. This is to say that during drying, the thermo-oxidative de-

NR/Carbon Black Masterbatch ...

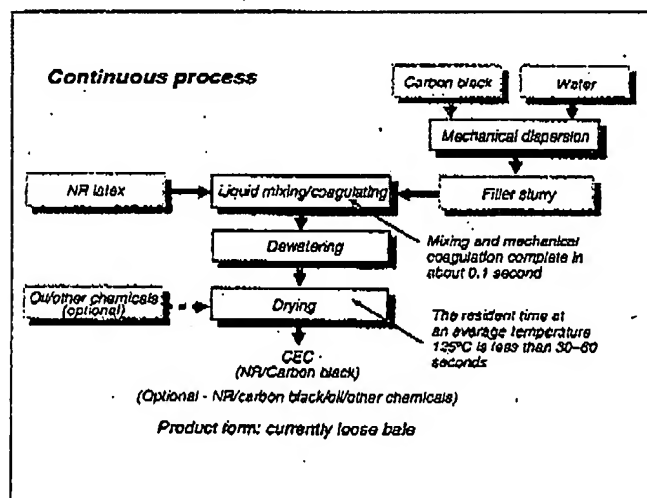


Figure 1. CEC process

duced as a stabilizer for storage. Optionally, the small ingredients in the compounds, such as zinc oxide, stearic acid, antiozonants, antioxidants, and wax can be added in this stage.

The dried material can then be slabbed, cut or pelletized. Currently, CEC is packaged into highly friable bale form consisting of compressed small strips.

The key feature of the CEC process is the fast mixing and coagulation, and a short drying time at high temperature. This achieves excellent performance for the material as polymer-filler interaction can be better preserved and polymer degradation can be well eliminated.

Mixing of CEC

One of the features of CEC is its superior filler dispersion. The dispersion of carbon black in the polymer is, therefore, not a concern for the compounders using CEC. Mixing other ingredients, such as antioxidants, wax, oil, vulcanization activators and curatives, requires distinct procedures to take full advantage of CEC's unique properties due to the different rheological behaviors and different requirements between conventional rubber and CEC. The exact mixing specifications will be dependent on the type of compounds, mixing equipment, desired downstream processability, product performance requirements, and other factors.

Features of CEC related to mixing

Mooney viscosity

CEC has a higher viscosity relative to pure polymer and the dry mixed masterbatch. The high viscosity of CEC is mainly caused by the hardening of the material during storage. This is especially the case for highly loaded compounds with high surface area carbon blacks, such as those used for tire treads. Besides the hydrodynamic effect of the filler, three mechanisms are responsible for the hardening effect of CEC: polymer gelation, bound rubber formation and carbon black flocculation. However, equilibrium is reached in a short period.

Polymer gelation – This is the same as that for pure NR hardening during storage [2]. In this mechanism, the condensation of the biochemically-formed aldehyde groups along the polymer chains, probably via association with non-rubbers, gives rise to increased viscosity of the rubber. A similar effect should be evident in CEC.

Bound rubber formation – This mechanism is related to the addition of carbon black in the polymer resulting in adsorption of polymer chains on the filler surface. This process may continue during storage as in the case of dry mixing where the bound rubber increases rapidly at the beginning of storage and reaches equilibrium in about 1 month [3]. The formation of bound rubber will significantly

ments on the filler surface. It is also related to the entanglement between the adsorbed polymer chains and polymer molecules in the matrix (50).

Carbon black flocculation – It has been recognized that through filler-filler interaction filler flocculation or agglomeration can take place during storage. This is especially true at the very early stage of storage when the bound rubber has not been fully developed. As a consequence, the rubber trapped in the agglomerates will lose, at least partially, its identity as rubber and behave as a filler due to its immobilization as far as the agglomerates cannot be broken down under an applied stress [6]. This leads to a substantial increase in apparent volume fraction of filler, hence viscosity of the compound.

The storage hardening effect of pure NR can be efficiently inhibited by using some chemicals, such as hydroxylamine, which can react with aldehyde groups on the polymer chains via condensation mechanism [7]. However, due to the filler effect, effectiveness of these chemicals for preventing storage hardening of CEC is considerably reduced.

Bound rubber formation is an indicator of polymer-filler interaction, which is an important parameter that governs rubber reinforcement. Any attempt to reduce bound rubber formation will result in deterioration in rubber properties, abrasion resistance in particular.

It should be point out that when some small chemicals, such as stearic acid, antioxidants, oil and wax, are added in the CEC process, the viscosity of CEC will, to a certain extent, be reduced which facilitates the mixing process.

Mastication efficiency

A favorable feature of CEC related to mixing is that compared with dry-mixed carbon black masterbatch, the Mooney viscosity of CEC drops more rapidly upon mastication and during downstream processing. This may be associated with the high viscosity of CEC, which gives rise to high shear stress during mixing, facilitating the mechano-oxidative mastication and break down of agglomerates to release the trapped rubber. After mixing, easily

NR/Carbon Black Masterbatch ...

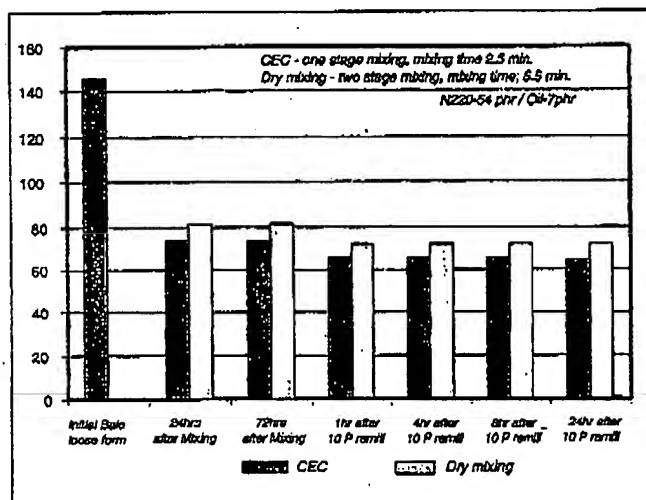


Figure 2. Effect of mixing in Banbury (1.6L) and remilling (5" roll mill) on Mooney viscosity

bilized, showing that the Mooney viscosity of the compound does not change with storage (Figure 2). As will be shown below, the rapid break down may lead to over mixing unless the mixing time is considerably reduced.

CEC product form

Generally, high torque may be generated when high viscosity materials are directly charged in to the Banbury. Practically, to avoid excess power or unacceptable peak torque, the materials are either warmed-up in a hot room or masticated on an open mill to reduce the viscosity. In order to simplify mixing procedures and minimize torque, CEC compounds are made into a "loose" bale form. In these loose bales, besides the bale can be easily broken down, there is a certain amount of void volume, which substantially reduces the peak power when the CEC bale is engaged between the rotors and wall of the mixer chamber in the early stage of breaking down the compound. This allows the loose bale to be fed directly into the Banbury without prewarming and premastication. Commercially, CEC is packaged in easy-to-handle 16 kg loose bales in low melt bags. Product form alternatives, such as slabs or pellets, are also under evaluation.

Mixing equipment

There are broadly two types of batch in-

design, the main difference between these two types of mixers is whether the rotation paths of the major diameters of the two rotors intercept or not. The features of the tangential Banbury are a large available mixing chamber volume, high fill factor, quick feeding and discharging of material and high productivity per energy input [8]. The intermeshing mixer has the following advantages: efficient mastication, temperature control, incorporation of oily material and dispersion of ingredients. Therefore, similar to dry mixing, when different mixers are used for CEC mixing, the operational parameters, such as the fill factor, material feeding, rotor speed, ram pressure, and mixing cycle must be adjusted accordingly.

In addition, CEC can be pelletized in a free flow form. The pellets can be easily fed to the continuous mixer to facilitate the continuous mixing.

Mixing procedures

Similar to conventional mixing, the mixing of CEC consists of several phases. After feeding in the internal mixer, the CEC material is broken down and masticated for a short period of time. This is followed by the addition of the small chemical ingredients such as cure activators, antioxidants, wax, and oil. Generally the batch is dumped after addition of the small chemicals and the curatives are added in the following or second stage. This is referred to as two-stage mixing. In certain in-

Two-stage mixing

CEC mastication - After charging CEC into the mixer, the mastication of CEC prior to the incorporation of other ingredients is critical. In this step, the material viscosity drops substantially which is essential for chemical addition and downstream processing. The length of mastication is mainly determined by the target Mooney viscosity, which should target downstream mixing and processing. For tire tread compounds, for example, when a cold-feed extruder is used, a slightly longer mastication period is favorable for the extrudate quality. The mastication time is also related to the incorporation period and dispersion of other ingredients. Depending on the type of equipment, rotor speed, and compound, the mastication time can vary from 30 to 90" and small adjustments may be necessary when the batch size and ram pressure are changed.

Addition of small ingredients and oil - Following the initial mastication period, for CEC only having rubber and carbon black, the small ingredients, such as zinc oxide, stearic acid, antioxidants and wax can be added. Generally, there is no significant difference in the incorporation and dispersion of unmelttable powder chemicals between dry mixing and CEC mixing. However, the behavior of oily materials is somewhat different. This includes oil, liquid chemicals and solid materials that melt at the mixing temperature such as stearic acid, wax and some antioxidants. When oily materials are added, the stretching and tearing of the batch by the tips of wings no longer occurs. Therefore, no material transfer takes place between the rotors and between the rotors and chamber side surfaces, hence no energy is imparted into polymer matrix. The oily materials essentially behave as a lubricant. The mixing action does not start until the oily materials are absorbed into the rubber. Therefore, the lubrication time or incorporation time of oily materials is determined by the rate of their absorption in rubber.

In practice, an increase in mastication time leads to shorter lubrication time. In a limited range, an increase in batch size also results in speeding up the incorpora-

NF/Carbon Black Masterbatch ...

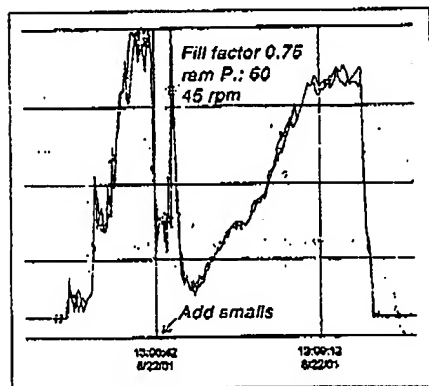


Figure 3. Typical CEC mixing power in F270 Banbury

when the mastication temperature is relatively higher and an increase in rotor speed, if allowed, can effectively reduce the lubrication time. Shown in Figure 3 are mixing charts for CEC with 50 phr N234 in a F270 Banbury.

After the incorporation of the ingredients, the batch can be dumped either onto a roll mill or into a single or twin screw extruder for further blending, cooling and sheeting or pelletizing, which are similar operations to those of dry mixing.

When the oily chemicals are added in CEC production process, the mixing is facilitated due to reduced viscosity and elimination of lubrication. For CEC containing all small ingredients, except curatives, this stage of mixing is only for mastication. Therefore, the mixing productivity can be significantly increased by pre-addition of oily chemicals. In a mixing trial, the lubrication time is reduced by about 0.5 to 1 minute for the CEC with pre-addition of stearic acid. This results in a reduction in the mixing cycle by about 25 ~ 30 % with Banbury F50-4WST and intermeshing mixer Intermix K-2A Mark 5 for the first stage compared with the CEC without stearic acid.

Second stage of mixing – For two stage mixing, the second stage is used mainly to add curatives. The mixing procedure is the same as that for dry mixing.

Single-stage mixing

Single stage mixing enhances productivity as the mastication, incorporation, and dispersion of all ingredients are com-

mixing time is allowed to achieve the required dispersion of the ingredients and adequate down stream processability. With single stage mixing, curatives can be added either with or after other ingredient addition. The batch should generally be dumped below a temperature limit of 125 °C to prevent pre-cure or scorch.

The key parameters to determine the feasibility of single stage mixing are, among others, the energy input and temperature profile. While enough energy is needed for ingredient dispersion and for bringing down the compound viscosity, the temperature has to be well controlled to a narrow range during and after curative addition for the safety of down stream processing, such as extrusion, calendaring or molding.

For mixers whose rotor speed cannot be adjusted during mixing and whose cooling system is not efficient enough, the mixer should run at lower rotor speed in order to keep the batch temperature in the appropriate range. For example, the rotor speed should be similar to that used in the second stage of a two-stage mixing procedure. Consequently, the mixing cycle should be longer than that of the first stage of the two-stage mixing, but shorter than a 2-stage mix.

The mixing efficiency can be substantially improved and the mixing cycle can be significantly reduced for single stage mixing when using a mixer with a variable speed drive and an intensive cooling system. In this case, the mastication and addition of small ingredients, except curatives, can be performed at high rotor speed. When the rotor speed is reduced the mixer can be used as a cooling unit to bring the compound temperature down to a limit in an acceptable time frame to allow the curative addition and dispersion. Intensively cooled machines can reach excellent cooling rates. In this regard, the intermeshing mixer exhibits a significant advantage over a tangential Banbury due to its high mastication efficiency and high contact area between the compound and the mixer temperature-controlled surface.

In addition, pre-addition of small chemicals in the CEC compound facilitates single-stage mixing. Additionally, this results from lower compound viscosity,

Total mixing cycle

The total mixing cycle, as mentioned before, is determined by the dispersion of the ingredients and target viscosity of the compound. Too short of a mixing cycle may lead to a high compound viscosity, which in the worst case will leave some unfully masticated materials in the compound, giving a rough extrudate appearance. This is especially critical when a cold feed extruder is utilized. In the case of hot feed extrusion, the compound can be further masticated on the roll mills during warming before extrusion so that the mixing cycle in the mixer may be reduced.

Over mixing of the compound will result in a very low Mooney viscosity. However, this will have a significantly negative effect on compound properties, viscoelastic properties in particular. More severe mechano-oxidation of the polymer may influence the aging resistivity. Also a low compound viscosity can facilitate the flocculation of the filler during vulcanization, resulting in higher hysteresis [9]. This will increase the rolling resistance when the compounds are used for tires, especially in tread compounds. On the other hand, where low viscosity is required, such as in wire skim compounds, CEC can be particularly advantageous.

Generally, the CEC mixing cycle can be 30 to 70 % shorter than the traditional mixing time, depending on the mixing procedures of dry mixing.

In summary, CEC is a unique material that can be easily mixed in conventional rubber mixing equipment. To make maximum use of its inherent qualities to improve productivity and to realize the performance benefits that result, the different mixing behaviors of CEC have to be recognized.

Dispersion of carbon black in CEC

One of the greatest advantages of CEC is the superior dispersion of carbon black in polymer. Shown in Figure 4 are the comparison of macro dispersion measured by means of optical microscopy for two carbon-black-N134-filled vulcanizates: one prepared with CEC using two-stage mix-

NR/Carbon Black Masterbatch ...

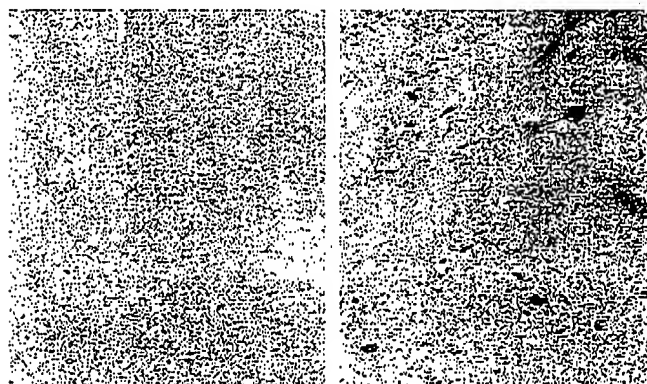


Figure 4. Dispersion of carbon black N134 in CEC and dry-mixed compounds

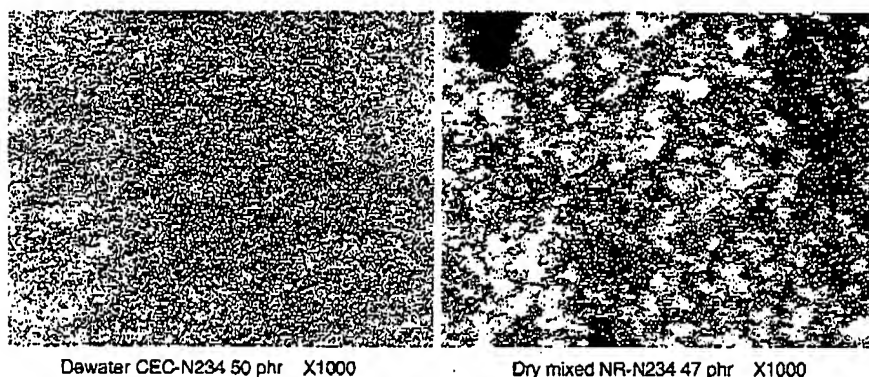


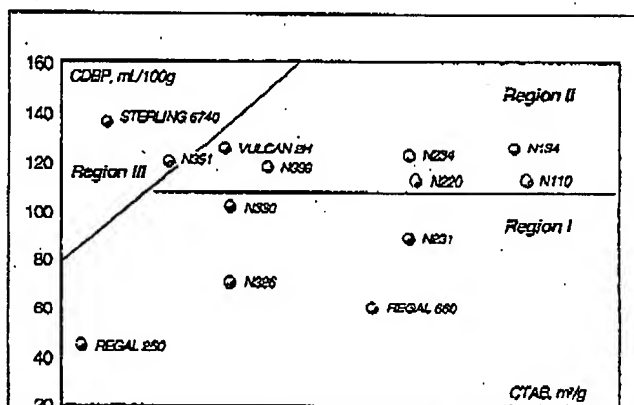
Figure 5. TEM images of dewatered CEC and dry mixed compounds

proved compared with that of dry mixed compound, even though energy input for CEC mixing is much lower. In fact, the carbon black dispersion and distribution are fully completed at the very early stages of CEC process. This can be demonstrated by an investigation of the carbon black dispersion of CEC with transmission electron microscopy. As shown in Figure 5, for the N234-filled CEC, the carbon black dispersion is already well dispersed and uniformly distributed throughout the polymer matrix in a very small scale after dewatering of the coagulum, where only minor mechanical energy has been input. In the case of dry-mixed compound, although an extensive mixing has been applied, the dispersion and distribution are still very poor. This suggests that high quality of filler dispersion can be achieved with CEC technology without significant mechanical breakdown of the polymer molecules.

For dry mixing, the carbon blacks can be classified into three groups corresponding to three regions in the DBPA-surface area map based on their dispersibility, as shown in Figure 6. The carbon blacks having low surface area and higher structure, Region III, are generally easy to

disperse with dry mixing. The dispersibility of those blacks in Region II is substantially reduced. The carbon blacks in Region I are low structure and high surface area products that are very difficult to disperse with the conventional process. However, with the CEC process, for all the carbon blacks investigated, either in Region I or Region II, the dispersion is substantially better than that for dry-mixed compounds. This is shown in Figure 7 where the dispersion of carbon blacks is characterized by percentage of undispersed area measured with a computerized imaging analysis system [10]. As can be seen, while excellent dispersion are shown for all CEC compounds with the undispersed area below 0.3 %, in the case of dry-mixed compounds, the undispersed areas are over a range from 0.6 to 7 % and from 1.5 to 10 % for Region II and I, respectively.

Technically, the grades of carbon blacks used for rubber reinforcement can be greatly expanded via CEC technology. Traditionally, as carbon blacks with surface area higher than 160 m²/g and CDBP lower than 60 mL/100g cannot be dispersed with dry mixing, they are not considered rubber grades. With CEC technology, however, over the practical range of loading, the carbon blacks with surface area as high as 260 m²/g and CDBP as low as 40 mL/100g can be dispersed in the polymer matrix with excellent dispersion. This is a great advantage of CEC technology for rubber reinforcement as these carbon blacks may impart some unusual properties to the filled rubber compounds.



NR/Carbon Black Masterbatch ...

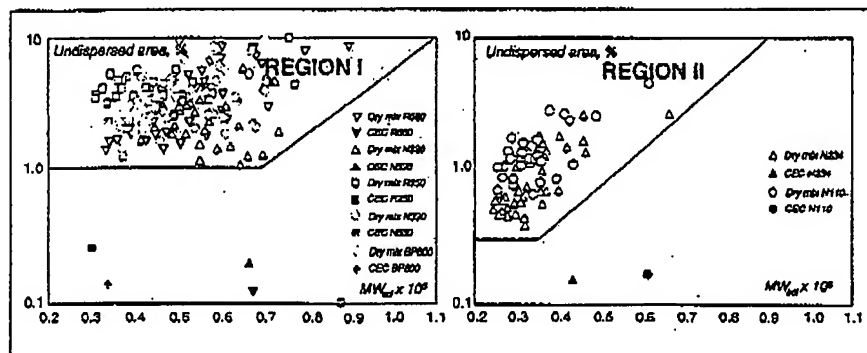


Figure 7. Dispersion of carbon blacks in CEC and dry-mixed compounds

Cure characteristics of CEC compounds

Generally, the cure characteristics of CEC compounds are similar to those of dry-mixed materials. However, somewhat shorter scorch time and higher cure rate may be observed with CEC compounds. This is generally due to the moisture content. It has been found that moisture can catalyze the decomposition of the accelerators into intermediate active products, for example, amine and 2-mercaptobenzothiazole from sulphenamide, the cure onset and cure kinetics can be significantly sped-up. The effect of moisture on cure characteristics is similar for both CEC and dry-mixed compounds. Presented in Figure 8 is the effect of moisture content on scorch time of N234 filled compounds. The moisture contents in the final compounds are varied either by adding moisture in the

compounds or by drying the NR and CEC in an oven before mixing and measured just before the scorch test. Obviously, the scorch time of both CEC and dry-mixed compounds follow almost the same function as moisture content. CEC's moisture content is 0.5 to 1 %.

Physical properties of CEC vulcanizates

Stress-strain properties

It is generally observed that, with the same formulation, the static moduli measured at high elongations (100 % and 300 %) of CEC vulcanizates are similar to those of their dry-mixed counterparts. Statistically, the CEC gives slightly higher tensile strength, longer elongation at break, and 1.5 to 2.5 points lower hardness at the practical loading.

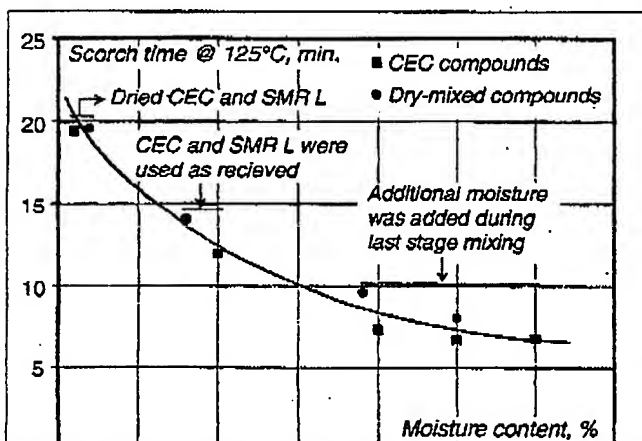


Figure 8. Effect of

Abrasion resistance

Generally speaking, for the carbon blacks that are easily dispersed, the abrasion resistance of CEC is comparable to that of dry mixed counterparts at lower loading. For the high surface area- and/or low structure-carbon blacks that have poor dispersibility, the CEC gives advantages over dry mixing in abrasion resistance, especially at higher filler loading.

Presented in Figure 9 is the effect of loading (carbon black N134) on abrasion resistance measured by means of Cabot Abrader (a Lambourn-type machine) at 7 % slip ratio. For both CEC and dry mixed compounds with SMR 20 that is generally used in tire tread, the abrasion resistance increases with filler loading, passing through a maximum, and then drops. Several mechanisms may be involved in the reduction in abrasion resistance at high filler loading. Among others such as reduction in rubber content, rapid increase in hardness, and deterioration of fatigue resistance, the poor dispersion of carbon black at high loading plays an important role for the decline of abrasion resistance. The excellent carbon black dispersion, even at high loading accounts for the significantly better abrasion resistance of CEC, compared with dry-mixed compounds at high loading. Also due to the improvement of filler dispersion, the CEC technology is able to move the maximum abrasion resistance and optimum filler loading to higher levels.

Practically, for certain applications, such as tire tread compounds, the hardness of the materials has to be limited in a relatively narrow range, due to the balance of wear resistance, skid resistance and other performance. For a given carbon black, this is generally achieved by adjusting carbon black loading and oil contents. It has been found that at constant hardness, the abrasion resistance follows different curves as a function of filler and oil loading. Figure 10 illustrates the effect of carbon black N234 and oil on abrasion resistance at 7 % slip ratio for the compounds with hardness of 65. For dry-mixed compounds, abrasion resistance decreases monotonously with increasing carbon black and oil loading.

NR/Carbon Black Masterbatch ...

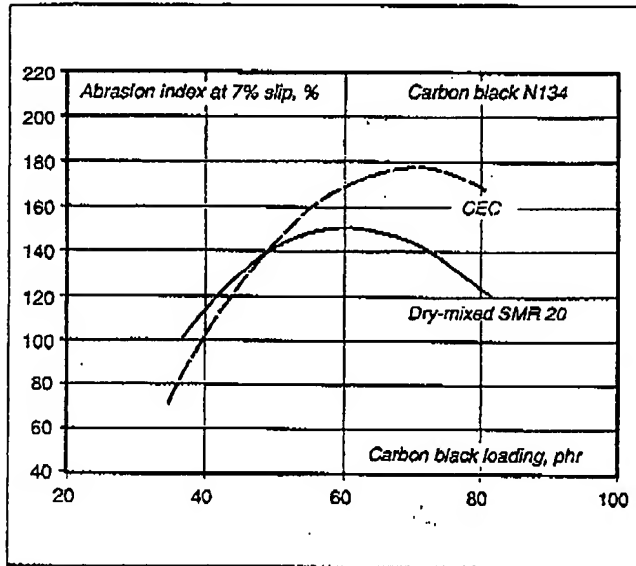


Figure 9. Effect of carbon black loading on abrasion resistance

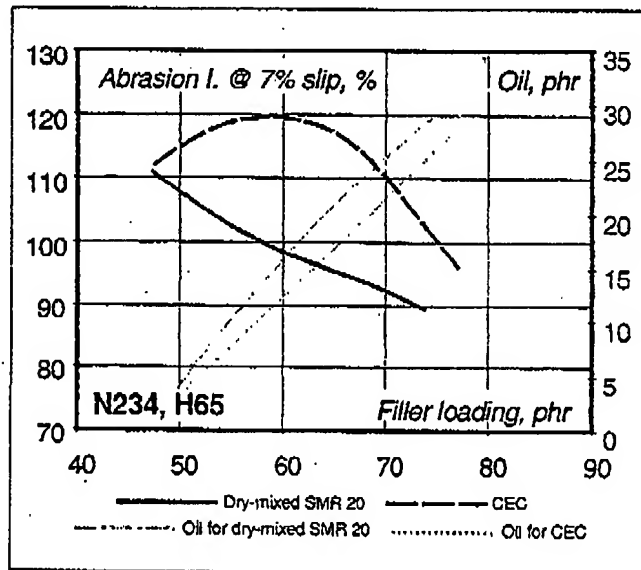


Figure 10. Effect of carbon black and oil loadings on abrasion resistance

of oil adsorption on polymer-filler interaction, one of the most critical parameters controlling abrasion resistance. In dry-mixed materials, the oil adsorption interferes with the polymer-filler interaction. In contrast, the polymer-filler interaction in CEC is much less affected by the addition of oil during mixing, as the adsorption of polymer chains on carbon black surface has already been completed. This can be demonstrated by evaluating the effects of oil addition on the bound rubber content. Figure 11 shows the differences in bound rubber content between CEC and dry-

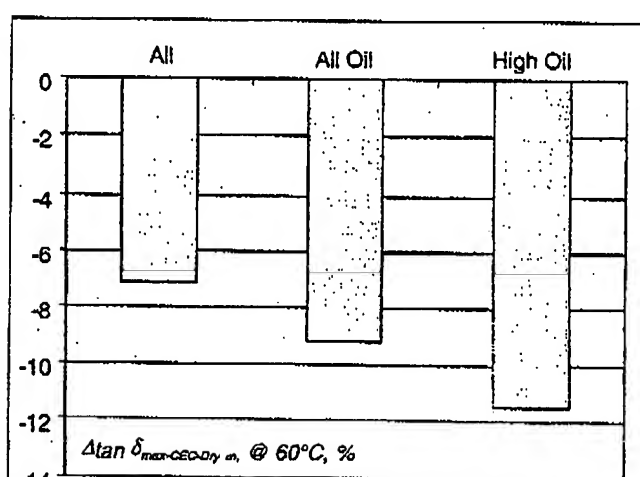
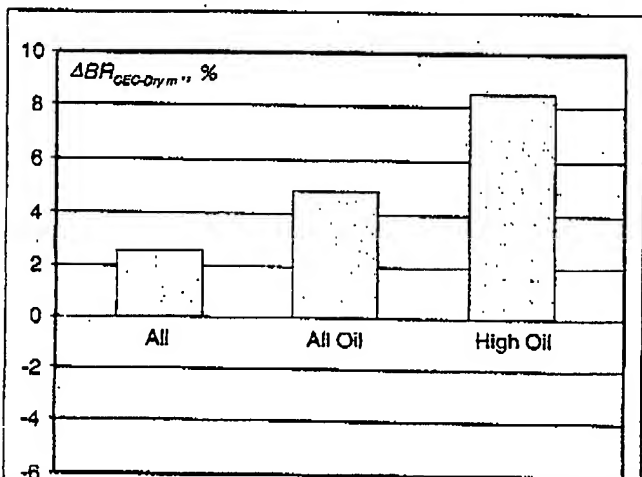
mixed compounds with different levels of oil. The results are taken from a statistical analysis of about 200 pairs, each pair having one CEC and one dry-mixed compound with the same formulation. For all compounds with and without oil, CEC gives higher bound rubber. The difference increases as the oil content increases for the compounds.

The drop in abrasion resistance of CEC compounds at high loading of oil and carbon black is mainly caused by the drastic reduction of the polymer content, the basic component in the vulcanizate.

Dynamic hysteresis at high temperature

One of the most important features of CEC vulcanizates is their lower hysteresis at high temperatures, such as 50 ~ 80 °C. Due to the excellent correlation between rolling resistance of tires and hysteresis of the tread compounds at high temperature, lower rolling resistance and lower heat build-up are expected with CEC.

For 8 carbon blacks including those with surface area from 110 to 200 m²/g



NR/Carbon Black Masterbatch ...

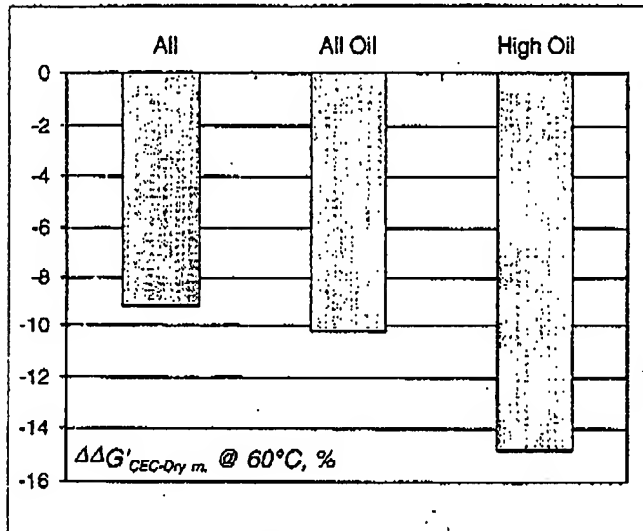


Figure 13. Effect of oil loading on Payne effects at 60°C

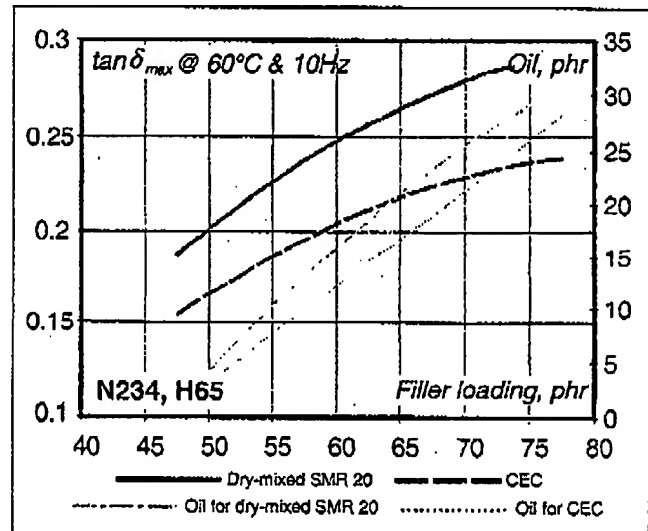


Figure 14. Effect of carbon black and oil loadings on hysteresis

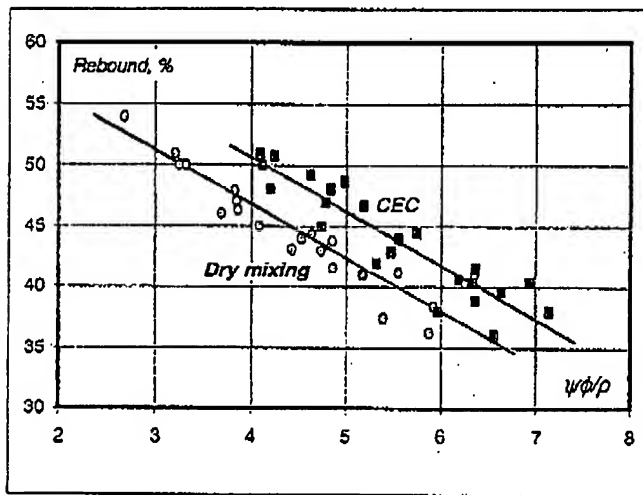


Figure 15. Rebound

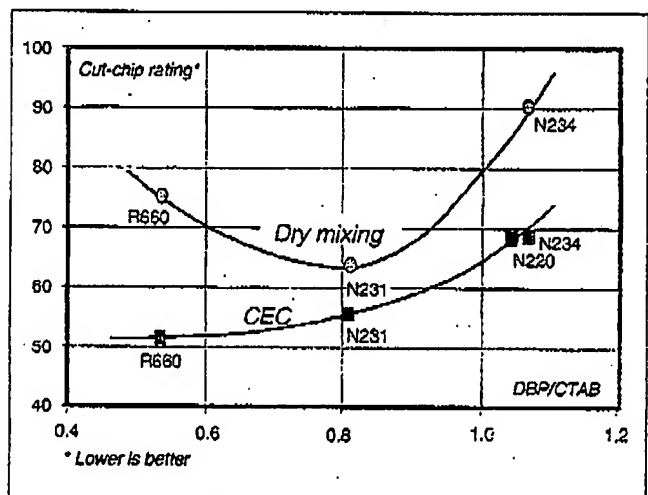


Figure 16. Cut-chip resistance

and CDBP from 52 to 116 mL/100g, compounds having oil loading from 0 to 30 phr and filler loading from 30 to 75 phr, the statistic reductions in maximum loss tangent obtained from strain sweeps, $\tan \delta_{\max}$, at 60 °C from 340 compounds are presented in Figure 12. When the hysteresis of the compounds is compared pair by pair between CEC and their dry-mixed counterparts with the same formulations, the hysteresis of CEC vulcanizates is on average 7 % lower. This number increases to 9 % and 11.5 % for the compounds containing oil (from 5 to 30 phr) and high oil (from 10 to

blacks, i.e., depressed filler networking. This can be demonstrated by the Payne effect, i.e., the difference in dynamic moduli measured at low strain amplitude and high strain amplitude. The Payne effect has been widely used as a measure of filler networking [6]. For all 340 compounds mentioned above, the average Payne effect measured at strain amplitude at 0.1 and 60 % is about 9 % lower for CEC vulcanizates (Figure 13) and this difference increases with increasing oil contents in the compounds.

Similar results were also observed when the compounds were adjusted to

is always lower for CEC and it is even more favorable at higher filler and oil loading.

The rebound results are consistent with the observations on hysteresis. In Figure 15, the rebounds measured with Zwick tester for a series of carbon blacks and filler loading are plotted as a function of $\psi\phi$, a so-called loading-interfacial-area parameter. Here ψ is interfacial area equaling to $pS\phi$. P is the density of the filler, S , the specific surface area and ϕ , the volume fraction of the filler in the compounds. Caruthers, Cohen and Medalia [11], found a good correlation between

NR/Carbon Black Masterbatch ...

compounds is improved by 3 % absolute points (or 5 % to 10 % in total) with CEC technology compared with conventional dry mixing.

The higher rebound or lower hysteresis of CEC compounds results in lower heat build-up. In a typical endurance test for CEC truck tires, compared to an existing commercial tire, the running temperature was reduced by 10 °C and endurance life increased by 17 % for CEC-tread compounds prepared with a comparable formulation as the dry mix.

Cut-chip resistance

The cut-chip resistance of CEC compounds were investigated by means of the Cabot OTR-Service Simulator with Nylon 6 ply rated 6.90 × 9 inch diameter tires. The tires were retreaded with compounds containing carbon black N234, N220, N231 and Regal 660 that is a low structure member of the N200 group of carbon blacks with surface area 112 m²/g and CDBP 52 mL/100 g. The cut-chip ratings were determined by counting and totaling the number of defects (1/8" or larger) in the tread area which result from cutting, chipping, chunking and abrasive action of the tire traveling over the Simulator track. The results are presented in *Figure 16*. Compared to the traditional materials, the CEC tread compounds give significantly improved cut-chip resistance. This is especially true for the low structure carbon blacks. It is generally observed that low-structure carbon blacks give higher

tearing strength, but this advantage is offset by their poorer dispersibility in dry mixing. For carbon black Regal 660, while cut-chip properties of dry-mixed compounds is even poorer than that of carbon black N231, its potential for improvement of cutting and chipping properties is fully brought out by CEC technology.

Flex fatigue

Mainly thanks to the excellent dispersibility of carbon blacks, and maybe also due to lower heat-build-up, a great benefit for fatigue resistance has been obtained from CEC. Compared with the traditional compounds, the average fatigue life in compression mode increases by well over 90 % which will impart a significant improvement to service life of some rubber goods, such as anti-vibration products, wipers, belts and even sidewall of tires.

Conclusions

Cabot elastomer composite (CEC) is the first filler-natural rubber masterbatch made with a continuous liquid mixing process. This technology enables an environment-friendly operation, simplified mixing and lower labor- and energy-consumption. A step improvement is obtained in filler dispersion. Superior dispersion of carbon blacks is now possible independent of filler morphologies. With this technology, the rubber grades of carbon blacks can be extended to those with much higher surface area and lower

structure grades, which cannot be dispersed in rubber with the traditional dry-mixing process. Due to the excellent dispersion of carbon blacks in CEC compounds, the hysteresis, stress-strain properties, cut-chip resistance, flex-fatigue life and abrasion resistance of the vulcanizates are significantly improved over their dry-mixed counterparts.

References

- [1] M.A. Mabry, F.H. Rumpf, J.Z. Podobnik, S.A. Westveer, A.C. Morgan, B. Chung and M.J. Andrew, USP 6,048,923 (2000, to Cabot Corporation).
- [2] M.J. Gregiry and A.S. Tan, Proc. Int. Rubber Conf., Kuala Lumpur, Vol. IV, p28.
- [3] J.L. Leblanc, Paper presented at IRC'98, 12 ~ 14, 1998, Paris, France.
- [4] H. Westlinning, Verstärkerfüllstoffe für Kautschuk, Paper presented at D.K.G., Oct. 3 ~ 6, 1962, Freiburg, Germany.
- [5] P.P.A. Smit, in "Le Renforcement des Elastomeres par les Surfaces Solides Ayant Une Action Renforçante", Colloques Internationaux du CNRS, No. 231, Paris, 1975.
- [6] M.-J. Wang, Rubber Chem. Technol., 71 (1998) 520.
- [7] P.S. Chin, J. Rubber Res. Inst. Malaysia, 22(1), 56.
- [8] N.O. Norrey, ACS Rubber Division, Nashville, Tennessee, Sept. 29-Oct. 2, 1998 Paper No. 70.
- [9] T. Wang, M.-J. Wang, J. Shell and N. Tokita, Kauts. Gummi Kunstst., 53, 497 (2000).
- [10] B. Chung, J. Menashi, B.E. Mackey and D.J. Curtis, Rubber World, p. 30, June (1997).
- [11] J.M. Caruthers, R.E. Cohen and A.I. Medalia, Rubber Chem. Technol., 49, 1076 (1976).

Corresponding author
M.-J. Wang
Cabot Corporation
Business and Technology Center
157 Concord Road
Billerica, Massachusetts, 01821-7001, USA